

## PATENT ABSTRACTS OF JAPAN

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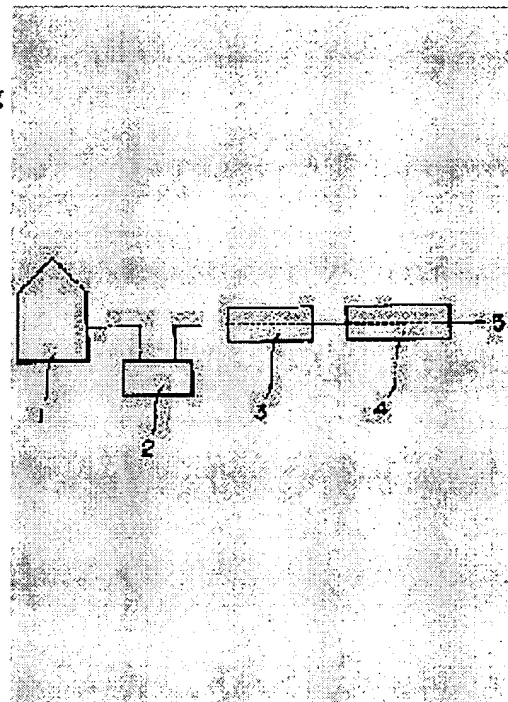
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## (54) CONTINUOUS PRODUCTION OF SYNTHETIC SILICATE CAPABLE OF SWELLING

## (57)Abstract:

PURPOSE: To efficiently produce a large amount of the silicate having a similar structure to a 3-octahedron smectite by subjecting a slurry prepared by blending various raw materials in a pipe reactor to continuous hydrothermal reaction at a specified temperature.

CONSTITUTION: Silicic acid and a magnesium salt or, in addition, an aluminum salt are blended to prepare a homogeneous mixed solution. The mixed solution is subjected to react with an alkaline solution to precipitate a silicon magnesium complex compound or a silicon magnesium aluminum complex compound. After the precipitate is separated, washed and condensed, lithium ion and/or a cation and, if needed, fluorine ion are added to obtain a slurry 1. Then, the above-mentioned slurry 1 is heated at 200-400°C in a pipe reactor to continuously produce the silicate 5 by a continuous hydrothermal reaction.



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**CLAIMS**

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[Claim(s)]

[Claim 1] The continuation manufacture approach of the synthetic bloating tendency silicate characterized by performing hydrothermal reaction for the slurry which blended, prepared and obtained various raw materials in compounding the synthetic bloating tendency silicate which has structure similar to a smectite continuously under conditions (200 degrees C thru/or 400 degrees C) within a pipe reactor.

[Claim 2] In compounding the synthetic bloating tendency silicate which has structure similar to 3-octahedron mold smectite The homogeneity mixed solution or the homogeneity mixed solution which blended the aluminum salt further of a silicic acid and magnesium salt, Silicon magnesium complex or silicon magnesium aluminum complex is built from an alkali solution. The quality of the byproduction dissolution is removed. This silicon magnesium complex or silicon magnesium aluminum complex Separation, after washing and condensing, The continuation manufacture approach of the synthetic bloating tendency silicate according to claim 1 characterized by performing hydrothermal reaction for a lithium ion and/or other cations, and the slurry that added and obtained fluorine ion when requiring continuously under conditions (200 degrees C thru/or 400 degrees C) within a pipe reactor.

[Claim 3] The homogeneity mixed solution of a silicic acid and magnesium salt is settled with an alkali solution. After filtration and rinsing remove the quality of the byproduction dissolution, a lithium ion, other monovalence cations, and the slurry that added and obtained fluorine ion when requiring Structure  $[\text{Si}_8\text{O}(\text{Mg}_{6-x-y}\text{Li}_x\text{Na}_y)_2\{(\text{OH})_{4-z}\}]_{(x+y)-(x+y)}\text{M}^+$  (setting the value of x, and y and z to  $0 \leq x \leq 2$ ,  $0 \leq y \leq 2$ ,  $0 < x+y < 2$ , and  $0 \leq z < 4$  here,  $\text{M}^+$  is monovalence cations, such as alkali-metal ion, ammonium ion, and alkyl ammonium ion.) The continuation manufacture approach of the synthetic bloating tendency silicate according to claim 1 which it has.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the continuation composition approach of the synthetic bloating tendency silicate which has structure similar to a smectite, and the synthetic bloating tendency silicate which has structure especially similar to 3-octahedron mold smectite in more detail about the continuation manufacture approach of a synthetic bloating tendency silicate.

[0002]

[Description of the Prior Art] There are a synthetic bloating tendency silicate which has structure similar to 2-octahedron mold smectite as a synthetic bloating tendency silicate which has structure similar to a smectite, and a synthetic bloating tendency silicate which has structure similar to 3-octahedron mold smectite. There are a montmorillonite, beidellite, nontronite, etc. as a synthetic bloating tendency silicate which has structure similar to 2-octahedron mold smectite, and hectorite, saponite, and a SUCHIBUN site are known as a typical thing of a synthetic bloating tendency silicate which has structure similar to 3-octahedron mold smectite. Although they exist also naturally, these have the approach of carrying out hydrothermal synthesis of the slurry which blended and prepared various raw materials as these synthesis methods, all are swollen underwater, it distributes, and are tintured with viscosity, and come to have cation-exchange ability. JP,63-6485,B is indicated as a process of the synthetic bloating tendency silicate which has saponite similar structure as a process of the synthetic bloating tendency silicate which has JP,63-6486,B and SUCHIBUN site similar structure.

[0003] on the other hand, the synthesis method of a hectorite mold clay mineral is main -- if a basis is carried out, three kinds of approaches as follows are learned.

(1) It dries, after Newman's adding the water solution which contains a sodium carbonate and water glass in the hydrothermal solution containing magnesium sulfate and a lithium chloride, making it react with elevated-temperature high pressure in an autoclave after he does reflux boiling of the system containing sediment, filtering and rinsing a reaction mixture and removing a byproduction salt, and the Hekla Ito mold silicate is compounded (Barbara Susan Newman, JP,46-813,B).

[0004] (2) Kondo makes an aqueous ammonia solution and a magnesium salt water solution react. Add a sodium silicate water solution to the generated magnesium-hydroxide slurry, and a magnesium-hydroxide-silica gel compound precipitate object is built. The lithium ion after performing filtration and rinsing and distributing water except for a byproduction electrolyte, Other alkali-metal ion or fluorine ion are added, hydrothermal reaction is carried out at 100-270 degrees C, a product is dried, and the hectorite mold silicate is compounded (Kondo 32, JP,51-33080,B).

[0005] (3) Torii etc. settles the homogeneity mixed solution of a silicic acid and magnesium salt with an alkali solution. And fluorine ion is added. the lithium ion after filtration and rinsing remove the quality of the byproduction dissolution, and other monovalence cations, if it requires [general formula  $\text{Si}_8\text{O}(\text{Mg}_{6-x}\text{Li}_x\text{Na}_y)_20\{(\text{OH})_4\text{-Z FZ}\} (x+y) \text{--} (x+y) \text{M}^+$  (here -- x and y --) with structure similar to a hectorite mold clay mineral by performing hydrothermal reaction and subsequently drying under conditions (100 degrees C thru/or 300 degrees C) the value of z --  $0 \leq x \leq 2$  and  $0 \leq y \leq 2$  and  $0 \leq x+y \leq 2$  and  $0 \leq z \leq 4$  -- carrying out --  $\text{M}^+$  They are monovalence cations, such as alkali-metal ion, ammonium ion, and alkyl ammonium ion. The hectorite mold silicate is compounded (JP,61-12848,B besides Kazuo Torii).

[0006] However, by Newman's approach, a head end process is quite complicated, and when taking time amount and time and effort, since anions, such as a chlorine ion which does not involve, and carbonate ion, exist in the sodium ion and reaction of an overlarge in large quantities at the time of hydrothermal reaction, it

has the fault that the purity of the silicate to generate is not not much high. And in order to remove the byproduction salt generated in large quantities after reaction termination by filtration and rinsing, it also has the fault from which a generation silicate swells and distributes and filtration and rinsing become very difficult. [0007] Moreover, although the fault of Newman's approach is canceled by Kondo's approach in order to perform hydrothermal synthesis after building a magnesium-hydroxide-silica gel compound precipitate object, filtering and rinsing and removing a byproduction salt After the magnesium-hydroxide-silica gel compound precipitate object of a raw material having trickled the magnesium salt water solution slowly into aqueous ammonia and making a magnesium hydroxide generate, In order to drop a water glass water solution slowly, to build and stir a magnesium-hydroxide-silica gel compound precipitate object and to make it homogeneity, It has the fault that pretreatment takes time amount and time and effort also in this case, and the fault of taking long duration considerably for bloating tendency clay to generate moreover at the time of hydrothermal synthesis is also accepted.

[0008] It is an advantageous approach at the point that conquer the fault of the approach of Newman or Kondo and the silicate which has structure similar to the hectorite which has the outstanding cation-exchange ability or gel organization potency is obtained comparatively for a short time, by using the homogeneous-precipitation object which acquired the approach of torii etc. from the mixed solution of an isolation silicic acid and magnesium salt on the other hand as a start raw material.

[0009] However, in manufacture of the synthetic bloating tendency silicate which has structure similar to 3-octahedron mold smectite, all hydrothermal reaction after raw material preparation is performed by the batch type approach by the manufacturing method currently indicated conventionally also including the approach of torii etc. And although it is said that the reaction temperature in that case is 100-350 degrees C and it is said, the reaction time of about 3 - 10 hours is required before and behind 180-250 degrees C in practice. [ reaction time ] [ 1 - 24 hours ] Moreover, although it is necessary to raise the slurry concentration taught to an autoclave as much as possible if it is going to manufacture the hydrothermal synthesis object obtained economically, if slurry concentration is raised too much, viscosity will become large (viscosity increases very much as a reaction progresses), equalization by stirring becomes difficult, and the quality and purity of a product fall.

[0010] However, it is necessary to make slurry concentration as high as possible (the higher possible one of slurry concentration of about 2 - 20% is desirable), and considering the desiccation process after hydrothermal synthesis, for this reason, troublesome handling called the draw of a quantity viscosity slurry is also needed. When the proof-pressure reaction container large-sized to it is very expensive and stirring of the slurry of further high viscosity took into consideration that it was very difficult for high torque etc., batch type hydrothermal reaction is unsuitable for mass production method, this has become one of the main factors of manufacturing-cost quantity, and an appearance of this solution approach was desired strongly.

[0011]

[Problem(s) to be Solved by the Invention] This invention solves the trouble of the conventional batch type hydrothermal-synthesis reaction adopted when carrying out hydrothermal synthesis from a preparation raw material, and offers the approach of carrying out continuation manufacture of the product excellent in quality and purity economically for a short time at insurance in manufacture of the synthetic bloating-tendency silicate which has structure similar to a smectite, and the synthetic bloating-tendency silicate which has structure especially similar to 3-octahedron mold smectite.

[0012]

[Means for Solving the Problem] As a result of inquiring wholeheartedly in view of the above-mentioned technical problem, by performing a hydrothermal synthesis reaction continuously by high temperature within a pipe reactor, this invention person etc. could mass-produce, found out that the sharp fall of a manufacturing cost was possible, and reached this invention.

[0013] In compounding the synthetic bloating tendency silicate which has structure similar to a smectite, claim 1 of this invention is the continuation manufacture approach of the synthetic bloating tendency silicate characterized by performing hydrothermal reaction for the slurry which blended, prepared and obtained various raw materials continuously under conditions (200 degrees C thru/or 400 degrees C) within a pipe reactor.

[0014] In claim 2 of this invention compounding the synthetic bloating tendency silicate which has structure similar to 3-octahedron mold smectite The homogeneity mixed solution or the homogeneity mixed solution which blended the aluminum salt further of a silicic acid and magnesium salt, Silicon magnesium complex or silicon magnesium aluminum complex is built from an alkali solution. The quality of the byproduction

dissolution is removed. This silicon magnesium complex or silicon magnesium aluminum complex Separation, after washing and condensing, It is the continuation manufacture approach of the synthetic bloating tendency silicate according to claim 1 characterized by performing hydrothermal reaction for a lithium ion and/or other cations, and the slurry that added and obtained fluorine ion when requiring continuously under conditions (200 degrees C thru/or 400 degrees C) within a pipe reactor.

[0015] Claim 3 of this invention settles the homogeneity mixed solution of a silicic acid and magnesium salt with an alkali solution. After filtration and rinsing remove the quality of the byproduction dissolution, a lithium ion, other monovalence cations, and the slurry that added and obtained fluorine ion when requiring Structure  $[Si_8O(Mg_{6-x-y}Li_xNa_y)_{20}\{(OH)_4-Z\}^{(x+y)-(x+y)}M^+]$  (setting the value of x, and y and z to  $0 \leq x \leq 2$ ,  $0 \leq y \leq 2$ ,  $0 < x+y < 2$ , and  $0 \leq z < 4$  here,  $M^+$  is monovalence cations, such as alkali-metal ion, ammonium ion, and alkyl ammonium ion.) It is the continuation manufacture approach of the synthetic bloating tendency silicate according to claim 1 which it has.

[0016] This invention is explained in detail below. This invention is aimed at all the hydrothermal synthesis reactions in manufacture of the synthetic bloating tendency silicate which has structure similar to a smectite. Naturally the hydrothermal synthesis reaction in manufacture of a synthetic bloating tendency silicate which has hectorite, saponite, and SUCHIBUN site similar structure also in it for manufacture of the synthetic bloating tendency silicate which has structure especially similar to 3-octahedron mold smectite serves as the object.

[0017] As hectorite, saponite, and a synthetic bloating tendency silicate that has SUCHIBUN site similar structure For example, the following matter indicated by JP,61-12848,B as matter which has hectorite similar structure,  $[Si_8O(Mg_{6-x-y}Li_xNa_y)_{20}\{(OH)_4-Z\}^{(x+y)-(x+y)}M^+]$  (here -- x --) The value of y and z is set to  $0 \leq x \leq 2$ ,  $0 \leq y \leq 2$ ,  $0 < x+y < 2$ , and  $0 \leq z < 4$ .  $M^+$  As matter which is monovalence cations, such as alkali-metal ion, ammonium ion, and alkyl ammonium ion, and which has saponite similar structure the following matter indicated by JP,63-6486,B, and a-(MgO) b-(aluminum  $2O_3$ ) c/2,  $[(SiO_2)(OH)_4-d-Fd]^{x-}$  and  $Mx/yy^+$  (here -- [-] -- inside -- a crystal-lattice component --) At least one ion which chose M from the group which consists of an alkali-metal cation, an alkaline earth metal cation, and ammonium ion,  $6 \leq a \leq 7.5$ ,  $4.5 \leq b \leq 6$ ,  $0.5 \leq c \leq 3.5$ ,  $0 \leq d \leq 4$ ,  $0.5 \leq x \leq 1$ ,  $1 \leq y \leq 2$  in which a, b, c, dx, and y have the following values, The following matter indicated by JP,63-6485,B as matter which has SUCHIBUN site similar structure, 8, a and  $(OH)_2/[ (SiO_2)_3 a+b-c-Fc]^{b-}$ , and  $Mb/yy^+$  (the value of a, b, c, and y in a formula is set to  $0 < a < 10$ ,  $0 < b \leq 1$ , and  $0 \leq c \leq 2/3 a+b$ , and  $1 \leq y \leq 2$ ) at least one cation which chose M from the group which consists of alkali-metal ion, alkaline-earth-metal ion, ammonium ion, and alkyl ammonium ion -- it is -- it is and the hydrothermal synthesis reaction in these manufactures is set as the object of this invention.

[0018] The slurry before the hydrothermal synthesis reaction of the synthetic bloating tendency silicate which has hectorite, saponite, and SUCHIBUN site similar structure in the above-mentioned patent official report, Namely, silicon magnesium complex or silicon magnesium aluminum complex is built from the homogeneity mixed solution or the homogeneity mixed solution which blended the aluminum salt further, and alkali solution of a silicic acid and magnesium salt. The quality of the byproduction dissolution is removed. This silicon magnesium complex or silicon magnesium aluminum complex Separation, after washing and condensing, Although a lithium ion and/or other cations, and the slurry that added and obtained fluorine ion are indicated by the detail and these slurries can be used in this invention if it requires The slurry used for the hydrothermal synthesis reaction set as the object of this invention is not limited to the contents indicated by these.

[0019] Moreover, naturally the hydrothermal synthesis reaction in manufacture of the synthetic bloating tendency silicate which has structure similar to 3-octahedron mold smectite indicated by the claim of JP,62-292615,A, JP,62-297210,A, and JP,63-182213,A is also set as the object of this invention.

[0020] In performing the hydrothermal synthesis reaction of these slurries, the description of this invention is changed into the batch type method currently carried out conventionally, and is that it processes continuously within a pipe reactor.

[0021] however, although the history of development of a continuous system autoclave and the hydrothermal synthesis reaction research using it is old and being gone back around 1930, there is a trouble of real operation top some and hydrothermal synthesis research of amelioration of the equipment and various compounds is done very enthusiastically by Yamasaki etc. after that -- having -- [-- a hydrothermal chemistry experiment service-message notice, pages 1-4, Vol.3, and No. -- 1 and 1979. \*\*\*\*\* 56-58, Vol.6, and No. -- 1 and 1986. 103 The

Nippon Mining meeting magazine, pages 519-523, 1194 ('87-8), The Japanese Society of Agricultural Machinery, pages 79-84, Vol.51, No.5 (1989), although JP,4-284886,A etc. is partly indicated also by] and domestic patent (JP,51-35390,B --) JP,2-5136,B, JP,51-145497,A, JP,54-10956,B, In compounding the synthetic bloating tendency silicate which has JP,54-10957,B, JP,62-260713,A, and structure similar to 3-octahedron mold smectite until now, there is no report of having performed the hydrothermal synthesis reaction of a raw material slurry continuously within the pipe reactor.

[0022] Although huge cylinder equipment is needed when it considers that mass production or extensive processing described above in the case of a batch type autoclave, the disruptive strength-ed to the internal pressure of a thick cylinder is not the thickness of a vessel wall, and is shown by the function of the ratio of a cylindrical bore and a cylindrical outer diameter. When performing extensive processing by the batch type, the container itself serves as the shape of a gun barrel of a gun as it becomes high pressure, and not only growing gigantic of the amount of capital investment but a safety engineering top trouble is large.

[0023] However, if a reaction rate is large when the hydrothermal synthesis reaction of a raw material slurry is continuously performed within a pipe reactor, a reaction is completed only by carrying out high-speed passage of the inside of the capillary heated by the elevated temperature, and there is possibility of extensive processing. it -- rise and fall of temperature, closing motion of a container, a raw material, and a product -- putting -- changing -- etc. -- time and effort is canceled and the merit of this point is also judged to be very large.

[0024] then, confirm that the product which a reaction be extremely complete for a short time by inquire wholeheartedly paying attention to the point say a point that this invention person be near the critical point ( 300 - 400 degrees C and 200 to 300 atmospheric pressure ) of water in various kinds of water solutions reaction, and a reaction rate increase remarkably, and perform the hydrothermal reaction of a raw material slurry continuously within a pipe reactor, and be obtain be satisfactory in respect of quality. Consequently, the fault of a batch type was canceled and a header and this invention were reached [ economical and that it can mass-produce advantageously also at a safety aspect, and ].

[0025] As stated above, the description of this invention is in the point of performing a hydrothermal synthesis reaction continuously by the pipe reactor. Although an example of the pipe-line system containing a pipe reactor is shown in drawing 1, of course, this invention is not limited to this. In this invention, it is important that the hydrothermal synthesis section consists of a pipe, and especially the system before and behind that is not limited. Moreover, the sense of a pipe can use a perpendicular direction or horizontal all, and can also give and use a fixed inclination. As for the pipe used for a pipe reactor, a straight pipe or a coil type pipe does not interfere, either.

[0026] In drawing 1, 1 is a raw material slurry tank, and the raw material slurry which sent the raw material into the heat exchanger 3, and was heated with the high-pressure metering pump 2 here performs a hydrothermal synthesis reaction in the state of heating with the following pyrogenetic reaction tubing (pipe reactor) 4, and acquires a resultant 5. The pyrogenetic reaction tubing 4 is an one-step type or a multistage type, and, of course, it is [ after passing a heat exchanger 3 ] also possible to arrange to several juxtaposition and to perform a hydrothermal synthesis reaction. Moreover, equalization of a slurry and promotion of a reaction can also be aimed at by preparing a spiral-type wing into the pyrogenetic reaction tubing 4, or preparing and stirring the wing for stirring. What is necessary is just to decide suitably by the production scale and the reaction condition, although about 1-10cm is suitable for the diameter of the pyrogenetic reaction tubing 4 and several m - 10m of an overall length of numbers are common.

[0027] Reaction temperature is judged that about 200-400 degrees C is suitable from the proof-pressure capacity of various kinds of test results and various equipments etc. Below 200 degrees C, a reaction rate is too small and there is a problem in the proof-pressure capacity of the various equipments which equipment internal pressure becomes high too much, and are constituted etc. above 400 degrees C.

[0028] Although the product 5 after a hydrothermal synthesis reaction is dried around 100 degrees C, grinding processing is carried out by the case and it is made a product, a desiccation process or later can also be skipped by the application. To in addition, the thing which a slurry becomes high viscosity extremely as a hydrothermal synthesis reaction progresses, the homogeneity of a slurry is lost even if it uses a powerful stirrer in the case of a batch type, and is easy to cause the fall of a reaction rate, the heterogeneity of a product, the fall of purity, etc. In the case of a pipe reactor, since a homogeneous slurry regime can be maintained at a thin pipeline through all the processes of hydrothermal synthesis by passing a slurry at the above speed to some extent, the aforementioned fault is improvable.

[0029]

[Effect] In carrying out hydrothermal reaction using the raw material slurry which blended, prepared and obtained various raw materials, in composition of the synthetic bloating tendency silicate which has structure similar to a smectite, and the synthetic bloating tendency silicate which has structure especially similar to 3-octahedron mold smectite, manufacture becomes possible continuously by changing into a pipe reactor the batch type autoclave adopted conventionally. Since it becomes possible to raise reaction temperature as proof-pressure equipment of an industrial production scale furthermore and is easy to maintain a homogeneous slurry regime through all the processes of hydrothermal synthesis, while being able to contribute to large compaction of reaction time, a homogeneous product is obtained by the high grade.

[0030] For this reason, the reaction time which the batch type took several hours is completed in several minute - number 10 minutes. So, it is fit for mass-producing with a small facility. Moreover, by carrying out \*\*\*\*\* passage of the thinner pipeline depending on the purpose, homogenization of much more slurry becomes easy and, for this reason, a homogeneous product can also be further obtained now by a rise and high grade of a reaction rate.

[0031] Although in the case of a batch type enlargement of a container is required for it if it is going to mass-produce to it, but the large-sized proof-pressure reaction container is very expensive, stirring of the slurry of high viscosity becomes very difficult because of high torque by enlargement further and an expensive agitator is needed, in the case of a pipe reactor, it can mass-produce with small equipment, and an installation cost also becomes cheap. moreover, rise and fall of temperature, closing motion of a container, a raw material, and a product -- putting -- changing -- etc. -- it cancels and the merit of time and effort of this point is also very large.

[0032]

[Example] Although an example explains this invention further below at a detail, unless it deviates from the main point of this invention, it is not limited to an example. next, [structure  $\text{Si } 8\text{O}(\text{Mg}_{6-x-y}\text{Li}_x\text{Na}_y)_2 20 \{(\text{OH})_4\text{-Z FZ}\} (x+y) \text{--}(x+y) \text{M}^+$  (here -- x --) similar to the hectorite mold clay mineral expressed with the following general formula the value of y and z --  $0 \leq x \leq 2$  and  $0 \leq y \leq 2$  and  $0 \leq x+y \leq 2$  and  $0 \leq z \leq 4$  -- carrying out --  $\text{M}^+$  They are monovalence cations, such as alkali-metal ion, ammonium ion, and alkyl ammonium ion. The example of the hydrothermal synthesis of the bloating tendency silicate which it has is shown.

[0033] (Hydrothermal synthesis) 4l. of water is put into a 10l. beaker, 860g ( $\text{SiO}_2$  28 % of the weight, 209 % of the weight of Na, mole ratio 3.22) of No. 3 water glass is dissolved, and in addition, a silicic-acid solution is obtained at once, stirring 162g of sulfuric acids 95%. Next, magnesium chloride 6 hydrate [ $\text{MgCl}_2$  and  $6\text{H}_2\text{O}$ , and first class grade chemical (98% of purity)] 560g is dissolved in 1l. of water, and, in addition to a silicic-acid solution, a homogeneity mixed solution is prepared, and it is dropped in 5 minutes, stirring in 3.6l. of 2 convention sodium-hydroxide solutions. After filtering reaction homogeneity compound sediment obtained immediately and fully rinsing, the solution which consists of 200ml of water, and  $\text{Li}(\text{OH})$  and lithium-hydroxide 1 [ $\text{H}_2$  hydrate O] 14.5g was added, it considered as the shape of a slurry, and the sample for hydrothermal synthesis (raw material slurry) was created. The conditions shown in Table 1 dried and ground at 80 degrees C after the hydrothermal synthesis test, and the evaluation test of a product was performed. As evaluation of the quality of a product, cation-exchange ability (capacity) and apparent viscosity were measured, and the product of a batch type and continuous system was compared.

[0034] (Measuring method)

(1) cation-exchange-capacity (meq. / 100g): -- methylene-blue adsorption process (2) apparent-viscosity: -- water was made to distribute the sample for a test at 2 % of the weight, and apparent viscosity was measured by 6 revolutions per minute (shear rate  $5.58\text{sec}^{-1}$ ) using the rotational viscometer (Tokyo Keiki , Inc. Brookfield viscometer).

[0035] (Examples 1-5) Hydrothermal synthesis was carried out using the pipe-line system shown in drawing 1 . The bore of pyrogenetic reaction tubing used 14 or 3mm and a thing with a die length of 10,000mm. In addition, pyrogenetic reaction tubing contains neither a wing nor stirring equipment inside. The result of having measured the cation-exchange ability (capacity) and apparent viscosity of a product is shown in Table 1.

[0036]

[Table 1]

Example Reaction temperature Reaction time Cation exchange capacity Apparent viscosity (degree C) (minute) (meq / 100g) (Pa-s)

1 240-260 10 105 2.4 2 240-260 15 108 2.1 3 290-310 7 107 2.9 4 290-310 10 108 2.3 5 340-360 5 108 2.6

[0037] (Examples 1-4 of a comparison) Hydrothermal synthesis is carried out on the conditions shown in Table 2 using the 5l. batch type autoclave (with stirring equipment), and the result of having measured the cation-exchange ability (capacity) and apparent viscosity of a product is shown in Table 2.

[0038]

[Table 2]

Example of a comparison Reaction temperature Reaction time Cation exchange capacity Apparent viscosity  
(degree C) (minute) (meq / 100g) (Pa-s)

1	200	300	99	1.9	2	225	180	101	1.4	3	200	15	45	0.1	4	225	15	61	0.2
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[0039] The cation exchange capacity of examples 1-5 and the examples 1-4 of a comparison and the value of apparent viscosity show that the continuation synthetic compounds by the pipe reactor are more expensive than the thing of the usual batch type autoclave composition about the quality of a product. Moreover, since the product of the short examples 3-4 of a comparison of reaction time has cation exchange capacity and the very low value of apparent viscosity, it is still understood that a reaction is inadequate. Therefore, reaction temperature is further raised from the examples 1-4 of a comparison, and reaction time is understood that the effectiveness of this invention is large from the result of the examples 1-5 which made it still shorter than the examples 1-4 of a comparison, and were made to react continuously. In addition, although examined almost like [ composition / of the synthetic bloating tendency silicate which has structure similar to 3-octahedron mold smectites other than a hectorite mold clay mineral ] the above, though optimum conditions differed, the almost same reaction result was obtained. It is clear by performing hydrothermal reaction continuously under conditions (200 degrees C thru/or 400 degrees C) by the pipe reactor by the above that a good result is obtained.

[0040]

[Effect of the Invention] This invention can mass-produce the product excellent in quality and purity safely efficiently by offering the continuation manufacture approach of the synthetic bloating tendency silicate which has structure similar to a smectite, and the synthetic bloating tendency silicate which has structure especially similar to 3-octahedron mold smectite, and performing a hydrothermal synthesis reaction continuously by high temperature within a pipe reactor. Many troubles of the conventional batch type hydrothermal synthesis reaction adopted by the continuation manufacture approach of the synthetic bloating tendency silicate of this invention when carrying out hydrothermal synthesis from a preparation raw material are solved, and since the sharp fall of a manufacturing cost is possible, the utility value on industry is high.

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[Translation done.]



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 03/05506

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C01B33/00 C01B33/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 889 004 A (CLARIANT GMBH) 7 January 1999 (1999-01-07) claims 12,14,16 ---	1
X	EP 0 088 372 A (HOECHST AG) 14 September 1983 (1983-09-14) the whole document ---	1
A	EP 0 889 003 A (CLARIANT GMBH) 7 January 1999 (1999-01-07) the whole document ---	1-36
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 03, 28 April 1995 (1995-04-28) & JP 06 345419 A (KOOPU CHEM KK), 20 December 1994 (1994-12-20) abstract --- -/-	1-36



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 03/05506

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 432 770 A (LAPORTE INDUSTRIES LTD) 22 April 1976 (1976-04-22) the whole document ----	1-36
A	US 3 586 478 A (NEUMANN BARBARA SUSAN) 22 June 1971 (1971-06-22) the whole document ----	1-36
A	GB 1 213 122 A (LAPORTE INDUSTRIES LTD) 18 November 1970 (1970-11-18) the whole document -----	1-36